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ON THE DISSOLUTION VOLOCITY OF OXYGEN INTO WATER. PART II.

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Received June 26, 1930. Published August 28, 1930.

Introduction. The oxidation velocity of sodium sulphite solution by means of air was found to be independent of the concentration of sodium sulphite under certain conditions.[1] This experimental fact can easily be explained if we consider that the observed reaction velocity is no other than the dissolution velocity of oxygen into water.

From this consideration, it was described in the previous paper,[2] that the dissolution velocity of oxygen D and the velocity constant k, calculated as a zero-order reaction, can be expressed by the following equations.

$$D=\frac{1}{4}k\times 10^{-4} \quad \text{moles per minute.} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$D=\frac{60\alpha p}{\sqrt{2\pi MRT}}\left(\frac{Vl}{20ru}+s_0\right) \quad \text{moles per minute.} \quad \ldots\ldots\ldots \quad (2)$$

$$k=\frac{24\alpha p\times 10^5}{\sqrt{2\pi MRT}}\left(\frac{Vl}{20ru}+s_0\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where α = the ratio of the total number of the molecules of oxygen which enter into water and the total number of the molecules of oxygen which collide with the unit boundary surface per unit of time, the concentration of oxygen in the surface being kept to be zero.

p = the partial pressure of oxygen.

M = the molecular weight of oxygen.

R = gas constant.

T = absolute temperature.

V = the volume of the gas passed per minute.

l = the depth of the center of a bubble when it just leaves the exit.

r = the radius of a bubble.

u = the ascending velocity of the bubble.

s_0 = the surface area of the liquid which is in contact with the gas outside of the boundary surface of the bubbles.

(1) S. Miyamoto, this Bulletin, **2** (1927), 74; *Scientific Papers of the Institute of Physical and Chemical Research*, **7** (1927), 40.

(2) S. Miyamoto and T. Kaya, this Bulletin, **5** (1930), 123.

If all the values in the equations 2 and 3 be kept constant except the value of p, the values of D and k can then be expressed by

$$D = A\alpha p \quad \ldots\ldots (4)$$
$$k = B\alpha p \quad \ldots\ldots (5)$$

If the value of α be independent of the partial pressure of oxygen,

$$D = A' p \quad \ldots\ldots (6)$$
$$k = B' p \quad \ldots\ldots (7)$$

where A' and B' are constants.

The present research was undertaken to ascertain if the present theoretical consideration be acceptable.

Experimental. The mixture of oxygen and air was passed through a narrow glass tube into the solution of sodium sulphite at uniform velocity and the oxidation velocity was observed.

The reacting vessel employed is shown in Fig. 1. The gas mixture, washed by acidified potassium bichromate solution and alkali, was passed at uniform velocity into the solution of sodium sulphite contained in A, the total volume of the reacting solution being made to 40 c.c. in each measurement. After t-minutes, the gas current was stopped and the stopcocks B and D were opened and the total quantity of the solution was poured into C, which contains a known quantity of iodine solution acidified with hydrochloric acid. After A was repeatedly washed by water, the vessel C was taken out, and the excess of iodine was titrated back by means of sodium thiosulphate solution, v in the following tables being the volume of sodium thiosulphate solution of 0.1000 normal, equivalent to the amount of sodium sulphite remained after the t-minutes passage of the gas mixture.

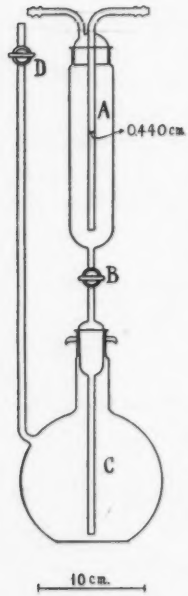

Fig. 1.

The experimental result shows that the oxidation velocity is independent of the concentration of sodium sulphite under the present conditions and the velocity constant k was calculated by

$$k = \frac{1}{t - t_0}(v_0 - v),$$

v_0 being the value of v at $t = t_0$. The values of $v_{calc.}$ were obtained by

$$v_{calc.} = v_0 - k(t - t_0)$$

using the mean value of k obtained experimentally.

The observed results are given in Tables 1 and 2, and graphically in Fig. 2. The partial pressure of oxygen, given in the first column of the Tables was calculated from the volumes of oxygen and air mixed.

Table 1.

Temp.=20°C. Velocity of Gas Passed=60.3 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.21	3	18.18	—	—
	43	11.87	12.06	0.158
	3	18.48	—	—
	33	13.78	13.89	0.157
	3	27.70	—	—
	33	23.06	23.11	0.155
	3	32.10	—	—
	33	27.46	27.51	0.155
	3	39.23	—	—
	43	33.12	33.11	0.153
	3	39.33	—	—
	39	33.80	33.82	0.154
	3	46.27	—	—
	43	40.10	40.15	0.154
	3	50.97	—	—
	43	44.97	44.85	0.150
	3	57.95	—	—
	33	53.46	53.36	0.150
	3	59.49	—	—
	43	53.69	54.37	0.146
	3	62.18	—	—
	33	57.59	57.57	0.153
				Mean 0.153

Table 1.—(*Continued*)

Temp.=20°C. Velocity of Gas Passed=60.3 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.33	3	25.30	—	—
	33	17.95	18.04	0.245
	3	38.82	—	—
	33	31.26	31.56	0.252
	3	53.66	—	—
	33	46.20	46.40	0.249
	3	60.39	—	—
	33	53.70	53.13	0.223
				Mean 0.242
0.48	3	24.37	—	—
	33	13.79	14.41	0.353
	3	35.46	—	—
	33	25.55	25.50	0.330
	3	49.51	—	—
	33	39.68	39.55	0.328
	3	63.40	—	—
	33	53.87	53.44	0.317
				Mean 0.332
0.60	3	26.18	—	—
	33	13.88	14.09	0.410
	3	37.70	—	—
	33	25.26	25.61	0.415
	3	50.68	—	—
	35	37.74	37.78	0.404
	3	64.34	—	—
	33	52.86	52.25	0.383
				Mean 0.403

Table 1.—(*Continued*)

Temp.=20°C. Velocity of Gas Passed=60.3 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.74	3	25.82	—	—
	33	10.74	11.06	0.503
	3	27.23	—	—
	33	12.37	12.47	0.495
	3	37.50	—	—
	33	22.46	22.74	0.501
	3	40.00	—	—
	33	25.60	25.24	0.480
	3	49.33	—	—
	34	33.74	34.08	0.503
	3	53.93	—	—
	33	39.17	39.17	0.492
	3	61.10	—	—
	33	46.85	46.34	0.475
	3	62.37	—	—
	33	47.85	47.61	0.484
				Mean 0.492
0.88	3	20.10	—	—
	23	8.60	8.74	0.575
	3	32.73	—	—
	33	16.43	15.69	0.543
	3	52.51	—	—
	33	35.25	35.47	0.575
	3	64.09	—	—
	33	46.77	46.05	0.577
				Mean. 0.568

Table 1.—(*Concluded*)

Temp.=20°C. Velocity of Gas Passed=60.3 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.97	3	22.88	—	—
	18	13.06	13.07	0.655
	3	23.58	—	—
	23	10.03	10.50	0.678
	3	29.75	—	—
	33	10.66	10.13	0.636
	3	32.32	—	—
	33	12.47	12.70	0.662
	3	33.22	—	—
	33	13.76	13.60	0.649
	3	37.79	—	—
	34	17.52	17.52	0.654
	3	39.28	—	—
	28	22.29	22.93	0.680
	3	43.73	—	—
	33	24.21	24.11	0.651
	3	44.01	—	—
	33	25.10	24.39	0.630
	3	49.09	—	—
	33	29.21	29.47	0.663
	3	52.36	—	—
	33	32.48	32.74	0.663
	3	55.51	—	—
	33	35.82	35.89	0.656
	3	60.90	—	—
	38	38.49	38.01	0.643
	3	63.46	—	—
	33	44.25	43.84	0.640
	3	65.72	—	—
	33	46.00	46.10	0.657
				Mean 0.654

Table 2.

Temp.=20°C. Velocity of Gas Passed=30.5 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.21	3	18.62	—	—
	53	13.79	13.77	0.097
	3	26.59	—	—
	54	21.67	21.64	0.096
	3	32.95	—	—
	53	28.09	28.10	0.097
	3	38.04	—	—
	53	33.11	33.19	0.099
	3	46.04	—	—
	53	41.21	41.19	0.097
	3	52.36	—	—
	63	46.58	46.54	0.096
	3	59.12	—	—
	53	54.29	54.27	0.097
	3	64.60	—	—
	63	58.80	58.78	0.097
				Mean 0.097
0.34	3	18.21	—	—
	33	13.51	13.59	0.157
	3	25.70	—	—
	43	19.72	19.54	0.150
	3	32.09	—	—
	43	25.81	25.93	0.157
	3	39.05	—	—
	33	34.56	34.43	0.150
	3	46.37	—	—
	53	38.65	38.67	0.154
	3	52.97	—	—
	33	48.30	48.35	0.156
	3	59.71	—	—
	43	53.51	53.55	0.155
				Mean 0.154

Table 2.—(*Continued*)

Temp.=20°C. Velocity of Gas Passed=30.5 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.46	3	18.72	—	—
	43	10.54	10.52	0.205
	3	23.68	—	—
	43	15.36	15.48	0.208
	3	39.43	—	—
	43	31.15	31.23	0.207
	3	45.42	—	—
	43	37.21	37.22	0.205
	3	52.88	—	—
	43	44.86	44.68	0.201
	3	65.96	—	—
	43	57.76	57.76	0.205
				Mean 0.205
0.59	3	18.56	—	—
	33	10.63	10.64	0.264
	3	23.64	—	—
	43	12.89	13.08	0.269
	3	32.29	—	—
	43	21.90	21.73	0.260
	3	45.69	—	—
	43	35.16	35.13	0.263
	3	51.81	—	—
	43	41.36	41.25	0.261
	3	58.74	—	—
	43	48.15	48.18	0.265
				Mean 0.264

Table 2.—(*Continued*)

Temp.=20°C. Velocity of Gas Passed=30.5 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.72	3	18.57	—	—
	26	11.25	11.30	0.318
	3	26.90	—	—
	33	17.33	17.42	0.319
	3	32.81	—	—
	33	23.21	23.33	0.320
	3	41.49	—	—
	43	28.83	28.85	0.317
	3	45.70	—	—
	43	33.10	33.06	0.315
	3	57.61	—	—
	43	45.07	44.97	0.314
	3	61.25	—	—
	43	48.79	48.61	0.312
	3	66.40	—	—
	43	53.95	53.76	0.311
				Mean 0.316
0.84	3	19.67	—	—
	34	8.44	8.42	0.362
	3	26.43	—	—
	33	15.46	15.54	0.366
	3	31.47	—	—
	43	16.79	16.95	0.367
	3	37.86	—	—
	43	23.47	23.34	0.360
	3	52.73	—	—
	53	34.38	34.48	0.367
	3	61.07	—	—
	33	50.30	50.18	0.359
	3	64.02	—	—
	53	46.09	45.77	0.359
				Mean 0.363

Table 2.—(*Concluded*)

Temp.=20°C. Velocity of Gas Passed=30.5 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.97	3	18.62	—	—
	23.5	9.98	10.05	0.424
	3	22.17	—	—
	35	8.92	8.79	0.414
	3	31.72	—	—
	43	14.98	15.00	0.419
	3	37.29	—	—
	44	19.99	20.15	0.422
	3	45.71	—	—
	43	28.98	28.99	0.418
	3	51.74	—	—
	53	31.11	30.84	0.413
	3	58.71	—	—
	43	41.92	41.99	0.420
	3	63.89	—	—
	53	43.07	42.99	0.416
				Mean 0.413

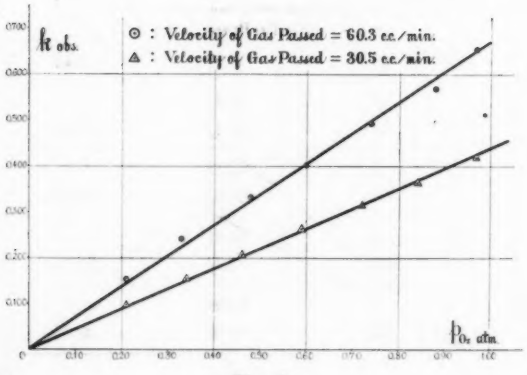

Fig. 2.

Table 3.

Temp.=20°C. Velocity of Gas Passed=60.3 c.c. / min.

p_{O_2} atm.	$k_{obs.}$	$k_{calc.}$	$D_{obs.}$ (Dissolution velocity of oxygen) moles / min.	$D_{calc.}$ (Dissolution velocity of oxygen) moles / min.
0.21	0.153	0.141	3.83×10^{-6}	3.51×10^{-6}
0.33	0.242	0.221	6.05 ,,	5.52 ,,
0.48	0.332	0.321	8.30 ,,	8.03 ,,
0.60	0.403	0.401	10.08 ,,	10.04 ,,
0.74	0.492	0.495	12.30 ,,	12.38 ,,
0.88	0.568	0.589	14.20 ,,	14.72 ,,
0.98	0.654	0.649	16.35 ,,	16.23 ,,

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Table 4.

Temp.=20°C. Velocity of Gas Passed=30.5 c.c, / min.

p_{O_2} atm.	$k_{obs.}$	$k_{calc.}$	$D_{obs.}$ (Dissolution velocity of oxygen) moles / min.	$D_{calc.}$ (Dissolution velocity of oxygen) moles / min.
0.21	0.097	0.092	2.43×10^{-6}	2.29×10^{-6}
0.34	0.154	0.149	3.85 ,,	3.72 ,,
0.46	0.205	0.201	5.13 ,,	5.03 ,,
0.59	0.264	0.258	6.60 ,,	6.45 ,,
0.72	0.316	0.315	7.90 ,,	7.87 ,,
0.84	0.363	0.367	9.08 ,,	9.18 ,,
0.97	0.418	0.424	10.45 ,,	10.60 ,,

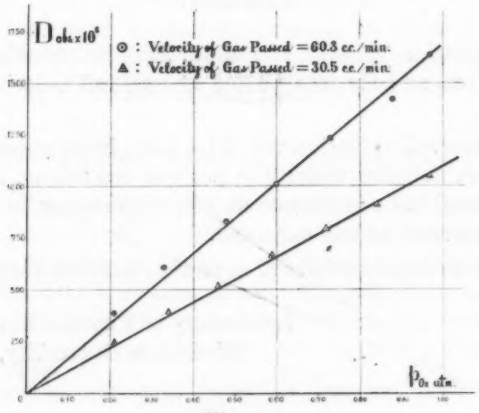

Fig. 3.

The values of $D_{obs.}$ in Tables 3 and 4 were calculated by the equation 1 using the observed values of k.

As will be seen in Tables 3 and 4 and in Figs. 2 and 3, the values of $k_{obs.}$ and $D_{obs.}$ can be expressed as a linear function of the partial pressure of oxygen of the gas passed. The values of $k_{calc.}$ and $D_{calc.}$ in the tables were calculated by the equations,

$$k_{calc.} = 0.669\,p$$
$$D_{calc.} = 16.73 \times 10^{-6}\,p$$

when the gas mixture was passed at the rate of 60.3 c.c. per minute, and

$$k_{calc.} = 0.437\,p$$
$$D_{calc.} = 10.93 \times 10^{-6}\,p$$

when the gas mixture was passed at the rate of 30.5 c.c. per minute.

The expectation was fullfiled; it was proved that the equations 6 and 7 can express the effect of the change of the partial pressure of oxygen on the velocity constant k or on the dissolution velocity D. The result confirms the author's consideration on the mechanism of this heterogeneous chemical reaction, described in the previous paper.

It was also verified that the value of α in the equations 2 and 3 can be regarded to be independent of the values of the partial pressure of oxygen of the gas mixture passed.

Summary.

(1) The oxidation velocity of sodium sulphite was observed when the mixture of oxygen and air was passed at uniform velocity under certain conditions.

(2) The observed oxidation velocities were independent of the concentration of sodium sulphite under the present conditions, and the velocity constant was found to be expressed as a linear function of the partial pressure of oxygen passed, as was expected.

(3) The theoretical interpretation on the observed result was given.

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STUDIES ON CATALYTIC ACTION AT HIGH PRESSURE AND TEMPERATURE.
CATALYTIC HYDROGENATION OF ETHERS.

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Received June 28, 1930. Published August 28, 1930.

The erroneous view that ethers are stable against chemical reagents and heat, which has been held by numerous chemists has been partly modified by the investigation conducted by K. Kashima[1] into the thermal decomposition of aliphatic ethers which are decomposed by being passed over heated Japanese acid clay, into the corresponding olefines and alcohols at low temperature (200°C.) and at high temperatures into olefines and water.

Ethers, by hydrolysis with HI, yield alcohols and iodides, which differ according to the temperature at which the ether is treated.

$$ROR' + HI \begin{cases} \nearrow RI + R'OH \\ \searrow RI + R'I. \end{cases}$$

According to P. Sabatier[2], ethers of the aromatic series, are reduced in the presence of reduced nickel to alcohols and hydrocarbons. As he says in his book, "Les oxydes aromatiques subissent sur le nickel une scission analogue, qui à deja lieu a température peu élevée pour le oxydes mixtes phenol-alcooliques, et diminue beaucoup le rendement dans leur transformation en oxydes mixtes cycloformeniques."

The authors undertook the present research in order to get some idea concerning the affinity of alkyl or some atomic groups for oxygen, from which they might elucidate the chemical nature of ethers.

I. Catalytic Reduction of Diphenylether.

Diphenyl ether prepared[3] from chlorobenzene and phenol shows m.p. 27.5°; b.p. 138° (21 mm.), $d_4^{25}=1.0712$; $n_D^{25}=1.5781$. In the experiment, a sample with reduced nickel which had been previously prepared from nickel oxide by reduction with hydrogen at 280° was placed in an autoclave of a capacity of 600 c.c. with compressed hydrogen. The autoclave, heated

(1) This Bulletin, **5** (1930), 25.
(2) P. Sabatier, "La catalyse en chimie organique," (1920), 186.
(3) F. Ullmann & P. Sponagel, *Ber.*, **38** (1905), 2211.

externally by electric resistance, was mounted horizontally on a shaking machine.

In the following table, the weight of the sample, the conditions under which the reaction was performed, the yield of the product and its physical constants are shown.

No.	Sample gr.	Reaction conditions			H_2 absorb. in mols.	Reaction product		
		Max. temp.	Initial press.	Time hours		Yield gr.	d_4^{25}	n_D^{25}
I	53	250°	60 atmos.	8	7.4	51	0.863	1.447
II	17	170°	60 ,,	6	5.4	17	0.918	1.476
III	50	220°	60 ,,	7	1.9	—	1.004	1.536

No. I.

	Fraction b.p.	Yield gr.	d_4^{25}	n_D^{25}	Remarks
1	73°–108°	21	0.779	1.427	Hexahydrobenzene
2	156°–168°	27	0.940	1.463	Cyclohexanol
3	Residue	2	—	—	

When purified, fraction 1 showed the constants: $d_4^{25}=0.7687$; $n_D^{25}=1.4248$, which agree with those for pure cyclohexane, and the 2nd fraction shows the constants ($d_4^{25}=0.9469$; $n_D^{25}=1.4635$) of pure cyclohexanol.

No. II.

	Fraction b.p.	Yield gr.	d_4^{25}	n_D^{25}
1	60°–110°	4	0.7795	1.4313
2	73°–115° (17 mm.)	7	0.9546	1.4712
3	115°–120° ,,	1	1.0092	1.5210

Fraction 1 and 2, as their physical constants indicate, are composed of cyclohexane and cyclohexanol respectively.

The third fraction, a mixture of diphenylether and dicyclohexyl ether, was fractionated to isolate the latter, which showed b.p. 230°–240°;

$d_4^{25}=0.9947$; $n_D^{25}=1.5080$; M.R.=54.51 (54.86 for $C_{12}H_{22}O$); and analytical results: C=79.1; H=12.1, (theory C=79.1; H=12.1% for $C_{12}H_{22}O$).

No. III.

	Fraction b.p.	Yield	d_4^{25}	n_D^{25}	Remarks
1	72°-84°	3	0.8162	1.4625	48% benzene, cyclohexane
2	75°-86° (14 mm.)	9	0.9551	1.4727	5% phenol+cyclohexanol
3	134°-138° ,,	19	1.0617	1.5702	diphenylether-cyclohexanol

Although diphenyl oxide[1] is said to be hardly susceptible to the catalytic action of reduced nickel in the presence of hydrogen, the conversion of the compound into cyclohexane and cyclohexanol ought to place with quantitative yield on heating it to 250° under 60 atmospheric pressures at 15°, in the presence of reduced nickel and hydrogen, in which disruption of the linking between carbon and oxygen will happen first and then the hydrogenation of the benzene nucleus of the molecules decomposed. This assumption was realized in experiment III, in which the reaction temperature was 220°, and accordingly the consumption of hydrogen is very small compared with that in the first experiment. The isolation of benzene and phenol together with their reduced substances from the reaction product is in favour of the above view. The occurrence of benzene in abundance is due to difficulty of hydrogenation under the experimental conditions, while phenol is hydrogenated with facility.

The other explanation of the formation of cyclohexane and cyclohexanol from diphenylether is shown in the scheme, in which

$$(C_6H_5)_2O \rightarrow (C_6H_{11})_2O \rightarrow C_6H_{11}OH + C_6H_{12}$$

hydrogenation of the benzene nucleus of the oxide takes place under the conditions, (lower temperature and high pressure) shown in experiment II.

The reaction products obtained from diphenyl oxide at high pressure and temperature in the presence of reduced nickel and hydrogen, are not entirely the same as those obtained by W. Ipatiew,[2] who conducted the experiment at 230° and under 100 atmospheric pressures in the presence of nickel oxide.

(1) A. Mailhe & M. Murat, *Bull. soc. chim.*, [4] **11** (1912), 122.
(2) *Ber.*, **41** (1908), 1001; *Compt. rend.*, **181** (1925), 793; refer W. Schrauth and W. Wege, *Ber.*, **57** (1924), 858.

II. Catalytic Reduction of Furfurol.[1]

1. Partial Hydrogenation of Furfurol. Reduction of furfurol was tried to see the behaviour of oxygen in ring, since furane forms a closely allied family with benzene from the standpoint of methods of formation and chemical behavior; the chain of four CH groups in the benzene molecule is closed as a ring by O.

M. Padoa and U. Ponti[2] performed the catalytic hydrogenation of furfurol at 190° by Sabatier's method, obtaining furfuryl alcohol with some α-methylfurane, α-methyl tetrahydrofurane, sec-n-amyl-alcohol and methyl propyl ketone, while at 270°, furane and CO were formed and these results are similar to these obtained by H. Pringsheim and H. Noth.[3]

Furfurol from Merck was used in the experiment after being purified ($d_4^{25}=1.153$; $n_D^{25}=1.522$).

(A) *Furfuryl alcohol.* (1) 50 gr. of furfurol were heated in the autoclave to 160°, with hydrogen under a pressure of 100 atmospheres, the reaction was completed with the absorption of 1 mol hydrogen in 6 hours, and the product ($d_4^{25}=1.132$; $n_D^{25}=1.498$) was fractionated:

	Fraction	Yield	d_4^{25}	n_D^{25}
1	70°–140°	3 gr.	0.984	1.504
2	70°–80° (28 mm.)	9	1.141	1.505
3	80°–97° ,, ,,	33 (80 %)	1.136	1.498
4	97°–183° ,, ,,	6	1.154	1.506
5	Residue	trace	—	—

The first fraction consisted of furane and methyl furane, and the second fraction of furfurol and furfuryl alcohol. The main component of the reaction product was assumed to be furfuryl alcohol and confirmed to be so by purifying with distillation under 17 mm. pressure: b.p. 74° (17 mm.); $d_4^{25}=1.1317$; $n_D^{25}=1.4928$; M.R.=25.15. Combustion: C=61.5; H=6.2%. Theory: C=61.3; H=6.1% for $C_5H_6O_2$. Phenyl urethane $C_{12}H_{11}O_3N$: m.p. 43°, N=6.4%.

(*B*) *Tetrahydro furfuryl alcohol.* In order to get the tetrahydro compound, 50 gr. of furfuryl alcohol were subjected for 7 hours to a partial

(1) The catalytic reductions in this part were conducted in the same autoclave and with a nickel catalyst which was prepared in the same way, as those in the former.
(2) *Chem. Zentr.* 1907, II, 570.
(3) *Ber.*, **53** (1920), 114.

hydrogenation which was carried out at around 180° and under an initial pressure of hydrogen of 85 atmospheres.

51 gr. of the product (d_4^{25}=1.062; n_D^{25}=1.455) were fractionated as usual and the physical constants of each fraction studied:

	Fraction	Yield	d_4^{25}	n_D^{25}
1	60°–140°	2.4 gr.	0.922	1.396
2	76°–90° (16 mm.)	21	1.052	1.450
3	90°–113° ,,	3.4	1.050	1.453
4	113°–200° ,,	11	1.101	1.463

The second and third fractions were assumed from their physical constants to be composed of the tetrahydro compound, which was isolated in the pure state by fractional distillation with a yield of 70%. B.p. 79° (17 mm.); d_4^{25}=1.0506; n_D^{25}=1.4509; M.R.=26.14. Combustion: C=58.8, 58.5; H=10.1, 10.1%. Theory: C=58.8; H=9.8% for $C_5H_{10}O_2$. Its phenyl urethane $C_{12}H_{15}O_3N$ (m.p. 56°[1]) gave N=6.3%, which agrees with theoretical value N=6.3 for $C_{12}H_{15}O_3N$.

(*C*) *Dihydro furfuryl alcohol.* Partial hydrogenation of 25 gr. of furfuryl alcohol at 144°, with hydrogen under a pressure of 80 atmospheres, was tried, and the product formed by absorbing about 0.8 mol of hydrogen showed the constants: d_4^{25}=1.084; n_D^{25}=1.470.

The product was fractionated into the following 5 parts:

	Fraction	Yield	d_4^{25}	n_D^{25}
1	50°–140°	0.5 gr.	—	—
2	77°–84° (18 mm.)	9	1.099	1.472
3	84°–90° ,,	5.7	1.098	1.472
4	90°–160° ,,	3.3	1.126	1.478
5	Residue	1.5	—	—

The second fraction seems to be a mixture of furfuryl alcohol and the tetrahydro-compound.

The third fraction was found to change its colour to yellow on exposure to air, with a characteristic odour; the physical constants of the purified

(1) H. Wienhaus, *Ber.*, **53** (1920), 1663.

sample were determined: b.p. 79–81° (14.5 mm.); $d_4^{25}=1.0986$; $n_D^{25}=1.4727$. M.R.=25.52 quite agrees with the calculated value 25.80 for dihydro furfuryl alcohol and the analytical results shows: Found: C=59.9, 60.3; H=8.4, 8.2%. Calc. for $C_5H_8O_2$: C=60.0; H=8.0%.

2. Complete Hydrogenation of Furfurol. *(A) Complete hydrogenation of furfuryl alcohol (No. II) and tetrahydro furfuryl alcohol (No. I).* The furfuryl alcohol was subjected to complete hydrogenation under the conditions described in the table, and the behavior of tetrahydro furfuryl alcohol (No. I) in the presence of reduced nickel and hydrogen at high temperature and pressure was also studied for comparison.

No.	Sample	Reaction			H_2 absorb. in mols.	Product		
		Temp.	Initial press. at 60°	Time in hour.		Yield	d_4^{25}	n_D^{25}
I	22 gr.	300°	30 atmos.	8	0.94	18.5 gr.	0.955	1.417
II	25 „	300	90 „	13	3.72	22.0 „	0.948	1.410

No. I.

	Fraction	Yield	d_4^{25}	n_D^{25}
1	64°–105°	9.2 gr. 58%	0.8864	1.398
2	70°–74° (12 mm.)	3.4 21	1.053	1.447
3	75°–110° „	3.3 21	1.039	1.449

No. II.

	Fraction	Yield	d_4^{25}	n_D^{25}
1	64°–100°	10.5 gr. } 71%	0.827	1.398
2	100°–140°	2.4 }	0.874	1.402
3	67°– 82° (15 mm.)	4.3 24	1.023	1.446
4	82°–105° „	1.0 5	1.015	1.448

A compound which was supposed to occur in the third fraction in No. I, as will be seen in experiment No. II, diminished in yield when the reaction

proceeded owing to transformation of the compound into substances of low boiling point. The molecular weight of the substance ($d_4^{25}=0.999$; $n_D^{25}=1.452$) isolated in a pretty pure state, in benzene solution by the cryoscopic method, was found to be 150, which corresponds approximately to the molecular weight of polymerized hydrofurfuryl alcohol or hydrofurfuryl ether $C_{10}H_{18}O_3$ (molecular weight 186).

Both the second fraction in No. I and the third fraction in No. II, were found to be composed of tetrahydrofurfuryl alcohol. The main portion of the reaction product, the first fraction in No. I and II, was again fractionated carefully into (I) b.p. 63–70°, (II) b.p. 76–82°, (III) b.p. 113°–130° and the following compounds were isolated:

(1) Tetrahydrofurane.—The fraction b.p. 63°–70°, which forms the main portion of the product, is a colourless liquid with a characteristic odour; $d_4^{25}=0.8669$; $n_D^{25}=1.4004$; M.R.=20.26. Combustion: Found, C= 66.0, 66.4; H=11.5, 11.5%. Calc. for C_4H_8O, C=66.7; H=11.1%.

(2) Methyltetrahydrofurane.—The second fraction b.p. 76–82°, shows $d_4^{25}=0.9325$; $n_D^{25}=1.4027$, which indicates that the fraction consists mostly of methyl tetrahydrofurane with some tetrahydrofurane. For reference, the combustion was carried out: C=68.6, 68.9; H=12.5, 12.4%. (Theory C=69.8; H=11.6 for $C_5H_{10}O$ and C=66.7; H=11.1% for C_4H_8O).

(3) n-Butylalcohol.—The fraction b.p. 113–130° ($d_4^{25}=0.8184$; $n_D^{25}=1.402$; M.R.=22.02) was assumed to be butyl alcohol. Combustion: Found, C=64.7, 64.3; H=13.7, 13.4%. Calc. for $C_4H_{10}O$, C=64.9; H =13.5%.

Its phenyl urethane melts at 54°. The attempt to detect amyl alcohol and also amylene glycol in the reaction product failed.

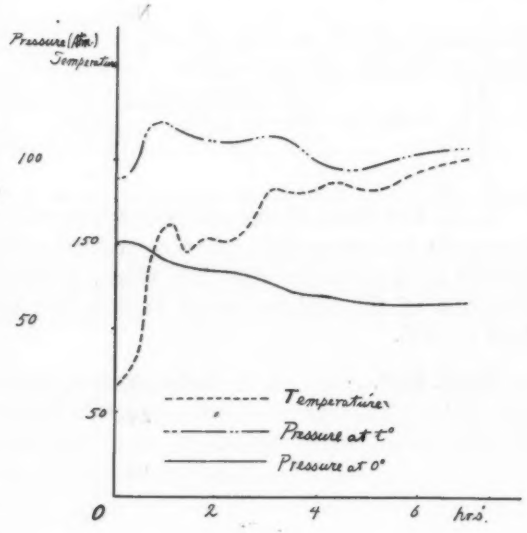
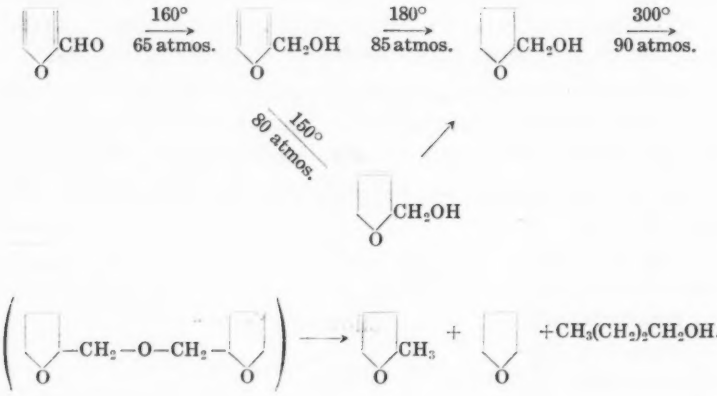


Fig. 1.

(*B*) *Complete hydrogenation of furfurol.* Furfurol was heated to 150° with hydrogen in the presence of the catalyst, under a pressure of 100 atmospheres; the pressure in the autoclave began to be depressed at 60°, and was kept constant after about one mol of hydrogen had been absorbed, the temperature being kept at 150°; it again showed the depression on the reaction temperature being raised, as is indicated in the figure.

Thus, the catalytic reduction of furfurol proceeds stepwise according to the temperature to which the reaction system is subjected.

The course of the chemical changes of furfurol on catalytic reduction in the presence of reduced nickel at high pressure and temperature is shown in the following scheme:



In the last phase of the reaction, tetrahydro furfuryl ether is assumed to occur as an intermediate reaction product which, owing to its instability towards heat or to the reducing agent, is immediately transformed by disruption of the carbon-oxygen linking into methyl furane, furane and butyl alcohol.

April, 1930.

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ON THE DECOMPOSITION OF METHANE, ETHANE AND ETHYLENE BY ELECTRIC SPARK.

By Chiko FUJIO.

Received July 12, 1930. Published August 28, 1930.

Berthelot[1] has already reported that methane decomposition by heat tends to form acetylene, ethane and hydrogen, in accordance with the following equations:

(1) $2CH_4=C_2H_2+3H_2$, (2) $2CH_4=C_2H_6+H_2$.

Ethane by heating yields ethylene, acetylene, methane, and hydrogen

(3) $C_2H_6=C_2H_4+H_2$, (4) $2C_2H_6=C_2H_2+2CH_4+H_2$

whilst ethylene tends to form ethane, acetylene and hydrogen,

(5) $C_2H_4=C_2H_2+H_2$, (6) $2C_2H_4=C_2H_6+C_2H_2$.

Acetylene was thus regarded by him as the ultimate decomposition product of hydrocarbons by heat.

The experiment for the decomposition of methane by the electric arc was carried out by W.A. Bone and D.S. Jerdan[2] and the gaseous products were noticed to be composed in the following proportion:

$C_2H_2 : H_2 : CH_4=9.8 : 85.6 : 2.5$.

and this ratio is maintained when acetylene is treated under the same conditions.

W.A. Bone and H.F. Coward[3] studied the decomposition of methane in the presence of porcelain at temperatures between 500° and 1200°, paying attention specially to the time factor for heating, and came to the following conclusions:—

(1) The rate of decomposition of methane in the presence of porcelain is appreciably below 700°, and for the most part it decomposed directly into carbon and hydrogen as postulated by M. Meyer and V. Altmeyer[4], and the process is probably reversible at all temperatures.

(1) *Compt. rend.*, **62** (1866), 905; **63**, 788.
(2) *J. Chem. Soc.*, **71** (1897), 41.
(3) *J. Chem. Soc.*, **93** (1908), 1197.
(4) *Ber.*, **40** (1907), 2134.

(2) The formation of acetylene and olefines could be detected only so long as the methane concentration exceeded 60%.

Lately R.C. Cantelo[1] has conjectured the possibility of the production of the higher hydrocarbons thermodynamically, such as ethylene and acetylene from methane by heating, and this assumption was supported by the experimental results arrived at by H.V. Wartenberg.[2]

Recently R.V. Wheeler[3] and F. Fischer[4] have independently studied the acquisition of benzene from methane.

According to the investigation of S.C. Lind on the exposure of methane to α-radiation, ethane and ethylene are formed and ethane and propane behave similarly to methane in forming saturated and unsaturated hydrocarbons resulting from the elimination of hydrogen or lower hydrocarbons which subsequently build up the higher members by addition or condensation as a result of valencies freed in the process.

On turning our attention to the molecular structure of methane, the infra-red absorption spectrum of methane have arrived at a tetrahedral structure of the methane molecule accepted already by chemists, but the experiments on the scattering of light, the absorption spectrum of the ultra-violet rays, and X-ray analyses are interpreted by numerous investigators in favor of the pyramidal structure which has been discussed by Weissenberg,[5] and the four valencies of carbon are not equivalent but consist of two different types, so that the six electrons of the carbon atom are distributed in three shells, two electrons in 1_1, 2_1, and 2_2 orbits, and accordingly the elimination of the hydrogen atom from the methane molecule should take place in succession, to form radicals of different reactivity.

$$CH_4 \longrightarrow -CH_3,\ =CH_2,\ \equiv CH,\ \equiv C.$$

Free radicals and hydrogen liberated from methane by heating or by radiating an α-particle, give a mixture of hydrocarbons still interacting since the reactions continue under further heating or radiation unless the products should be shifted from the sphere of the reaction system. As a matter of fact, the products so far studied in the thermal decomposition of methane, are so complicated by simultaneous and successive reactions to such a degree that only their broader aspects have been worked out.

(1) *J. Phys. Chem.*, **28** (1924), 1036.
(2) *Z. physik. Chem.*, **61** (1908), 366.
(3) *Fuel*, **7** (1928), 535.
(4) *Brennstoff-Chem.*, **9** (1928), 309.
(5) *Naturwiss.*, **15** (1927), 662; v. Henri, *Chem. Rev.*, **3** (1927), 189; J.K. Morse, *Proc. Nat. Acad. Sci.*, **14** (1928), 166.

Owing to the difficulty of interpreting the mechanism of reactions from these data, even with the accurate analysis of the products separated from the reaction product from time to time, the writer has undertaken the present investigation to study the chemical mechanism of the decomposition of methane by the electric spark, in which comparatively unstable products would be produced retarding the complex side reactions.

The apparatus employed in the experiment is shown in the accompanying figure (Fig. 1).

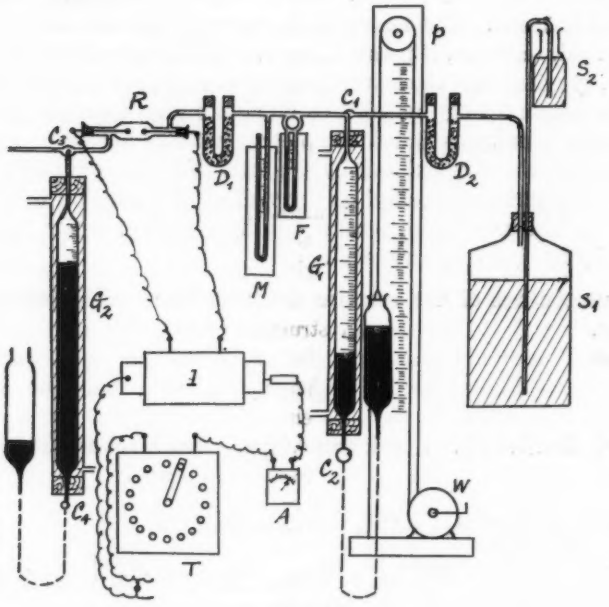

Fig. 1.

In the experiment, 100 c.c. of methane dried by passing into the dryers D_1 and D_2 containing calcium chloride, were passed into a reaction tube R the velocity being regulated with a flowmeter F and a manometer M; each reaction tube consists of a bulb of 1.5–3.5 cm. diameter and 2.0–7.0 cm. length, provided with spherical brass electrodes of 0.5–0.2 cm. diameter, and the sparks were produced between these electrodes by applying 110 volts D.C. with the aid of the induction coil I, to which the rheostat T and the ammeter A are connected. A receiver G of 150 c.c. capacity for the gaseous products is also connected to the reaction tube, which contained

mercury and was cooled with a water jacket to maintain a constant temperature.

As the gaseous products contain acetylene, ethylene, and hydrogen, as well as small quantities of heavy unsaturated hydrocarbons, special methods were adopted for their analysis. Acetylene was estimated with an absorbent in which 20 gr. of mercuric cyanide were dissolved in 100 c.c. of 2-N sodium hydroxide solution and saturated with ethylene and benzene, and for the estimation of ethylene another absorbent was used, composed of 20 gr. mercuric nitrate, 100 c.c. 2-N nitric acid saturated with sodium nitrate and benzene. The heavy hydrocarbons were estimated by fuming sulphuric acid. Ethane, if present, the sample being completely freed from acetylene, ethylene and the heavy hydrocarbons were subjected to oxidation with a palladium sponge at 100° to eliminate any hydrogen, the residual gas was subsequently exploded completely with an excess of oxygen, and the amount of ethane calculated by the ratio C/A[1] determined in the usual manner. The carbon deposited on the wall of the reaction tube was composed of carbon and some unsaturated hydrocarbon which can easily be dissolved by fuming sulphuric acid.

The percentage of the reaction products were calculated on nitrogen free bases.

Table 1.

Electrode dia. 1.0 cm. Spark gap 2.0 cm. Spark voltage 33,000 volts.

Gas velocity c.c./hour.	Percentage of decomposed CH_4	Percentage of gaseous products calculated for decomposed CH_4					Ratio of products
		Volume	H_2	C_2H_2	C_2H_4	C_2H_6	H_2/C_2H_2
510	74.7	187.6	150.3	32.7	2.7	1.2	4.60
513	79.0	203.2	163.3	34.9	3.0	1.3	4.68
926	65.5	193.2	157.9	33.2	2.0	—	4.79
963	57.4	195.4	160.7	31.7	2.3	—	5.07
1005	74.7	204.2	163.6	35.3	3.0	2.2	4.64
1360	57.7	196.9	163.7	34.9	2.9	—	4.69
1360	44.0	209.4	171.2	35.9	2.5	—	4.77
1578	58.6	194.9	160.1	32.9	2.3	—	4.87
1989	57.7	192.6	157.0	31.5	3.6	—	5.01
2070	48.6	192.7	157.2	30.7	1.8	—	5.12
	Mean	196.5	160.2	33.4	2.6	—	4.81

(1) C: contraction after explosion; A: absorbed volume.

The spark voltages in the experiments were calculated referring to those measured by Heydweiller[1] for various lengths of sparks between electrodes of various diameters at normal atmospheric pressure and temperature.

Table 2.

Electrode dia. 2.0 cm. Spark gap 2.0 cm. Spark voltage 47,000 volts.

Gas velocity c.c./hour.	Percentage of decomposed CH_4	Percentage of gaseous products calculated for decomposed CH_4					Ratio of products
		Volume	H_2	C_2H_2	C_2H_4	C_2H_6	H_2/C_2H_2
552	75.0	203.2	164.6	32.6	2.6	1.5	5.00
616	76.3	195.3	160.6	29.5	1.8	2.1	5.44
806	71.7	206.3	167.1	33.6	2.3	1.9	5.01
902	74.1	202.3	162.8	33.1	2.4	1.5	4.92
1181	77.4	204.2	168.4	33.0	2.0	—	5.10
1233	66.2	187.2	163.3	32.9	2.4	—	5.07
1396	63.8	201.7	166.1	33.5	2.4	—	4.97
1787	60.1	195.6	159.4	32.9	2.3	—	4.99
1916	62.1	200.4	164.7	33.0	2.0	—	4.99
	Mean	199.6	164.1	32.7	2.3	—	5.04

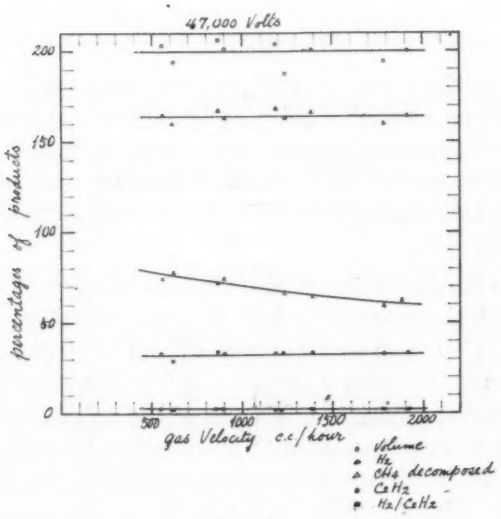

Fig. 2.

(1) J.A. Fleming, "The Wireless Telegraphist's Pocket Book," p. 109.

In Fig. 2, yields of acetylene and hydrogen, volume of the products, and ratio H_2/C_2H_2 are plotted against gas velocity. From these experimental results shown in Fig. 2, the decomposition of methane seems to occur at an uniform rate.

The following series of experiments were carried out at various spark voltages and results as mean value for each product are shown in Table 3.

Table 3.

Spark voltage (volts)	Spark gap (cm.)	Volume change of reaction gas calculated for decomposed CH_4	Percentage of gaseous products calculated for decomposed CH_4				Ratio of products
			H_2	C_2H_2	C_2H_4	C_2H_6	H_2/C_2H_2
8,000	—	178.3	138.2	30.0	0.9–5.8	0–6.7	4.78
20,000	1	185.0	150.0	33.5	7.0–8.0	—	4.80
23,000	2	183.0	145.0	30.0	3.2–9.8	0–17.1	5.03
23,700	3	188.2	150.0	33.8	3.0–5.6	0–2.5	4.46
24,000	4	192.1	155.4	31.8	2.7–4.4	0–1.3	4.73
33,000	2	196.5	160.2	33.4	1.8–3.6	0–2.2	4.81
47,000	2	199.6	164.1	32.7	1.8–2.8	0–2.1	5.04

The decomposition rate of methane was decreased inversely to gas velocity, while the production of acetylene remained constant, and the production of ethylene and ethane was decreased at high voltages. The yield of acetylene, consisting of about 30 % of the product, is immensely great in our case when compared with the result of the thermal decomposition of methane.

As regards the mechanism of the formation of acetylene from methane, the theory which seems to fit the fact, is to assume a temporary formation of the radical $-CH_3$ from methane by a collision of electrons in the process of the ionisation of the molecule, which will then be converted by destroying the electrical tension among the electrons of the radical, into radicals $\equiv CH$ and $\equiv C$ which will polymerise with one another to produce an electrical neutral molecule of acetylene and carbon, and also form methane by hydrogenation. The radicals $-CH_3$, $=CH_2$, in the same manner, would form, on the one hand, ethane and ethylene, and on the other, methane by hydrogenation.

Formation of radicals	Polymerisation	Hydrogenation
$CH_4 \rightarrow -CH_3+H$	$\rightarrow C_2H_6$	$\rightarrow CH_4$
$\rightarrow =CH_2+2H$	$\rightarrow C_2H_4$	$\rightarrow CH_4$
$\rightarrow \equiv CH+3H$	$\rightarrow C_2H_2$	$\rightarrow CH_4$
$\rightarrow \equiv C+4H$	$\rightarrow C_x$	$\rightarrow CH_4$

The decomposition of methane under a spark with considerably high voltage, will be shown by the equation,

$$3CH_4=C_2H_2+5H_2+C$$

in which two reactions were supposed to occur simultaneously.

$$CH_4 \rightleftarrows C+2H_2 \quad \ldots\ldots\ldots \text{(a)}$$
$$2CH_4 \rightleftarrows C_2H_2+3H_2 \quad \ldots\ldots\ldots \text{(b)}$$

When the electric spark voltage is very high or the gas velocity is very small, the reaction (a) is increased at the expense of ethane and ethylene.

The Decomposition of Ethylene and Ethane.

As will be understand in the foregoing theory for the formation of acetylene from methane, the radicals such as $-CH_3$ and $=CH_2$ were assumed to occur in the course of the transformation, which will result from the collision of electrons to produce $\equiv CH$, and for verification of this hypothesis which evidently demands production of the radical $\equiv CH$ by the action of an electric spark from $=CH_2$ and $-CH_3$ generated from a molecule of ethylene and of ethane, these gases were subjected to the action of an electric spark.

The ethylene used in the experiment was prepared by decomposition of ethylene-bromide (b. p. 130°–131.5°) with zinc powder, and washed by an alkali solution of pyrogallol to remove the oxygen in the gas. Ethane was also prepared by Grignard's method, that is, by the decomposition of ethyl magnesium iodide with water, and the generated gas was washed with fuming sulphuric acid, and the oxygen removed by contact with yellow phosphorus.

The results of the decomposition of ethylene are summarized in the following table.

Table 4.

Electrode dia. 1.0 cm. Spark gap 2.0 cm. Spark voltage 33,000 volts.

Gas velocity c.c./hour	Percentage of decomposed ethylene	Percentage of products calculated for decomposed ethylene				Ratios of products		
		Volume	C_2H_2	H_2	CH_4	C_2H_2/H_2	CH_4/H_2	CH_4/C_2H_2
754	85.2	196.7	56.2	132.4	6.7	0.43	0.05	0.12
798	81.0	200.0	58.4	133.4	6.6	0.44	0.05	0.11
1262	75.4	197.0	64.8	124.5	6.4	0.52	0.05	0.10
1609	74.3	198.9	64.4	127.2	5.5	0.51	0.04	0.09
1823	74.0	198.6	64.1	127.4	5.6	0.50	0.04	0.11
2170	71.0	196.5	61.0	124.6	4.3	0.49	0.04	0.08
2198	70.0	190.7	62.7	128.4	4.5	0.49	0.04	0.07
2651	60.4	190.0	67.8	124.1	5.3	0.55	0.04	0.08
2823	58.0	199.8	68.4	125.1	4.8	0.54	0.04	0.07
3115	58.0	188.8	63.1	122.4	3.4	0.52	0.03	0.05

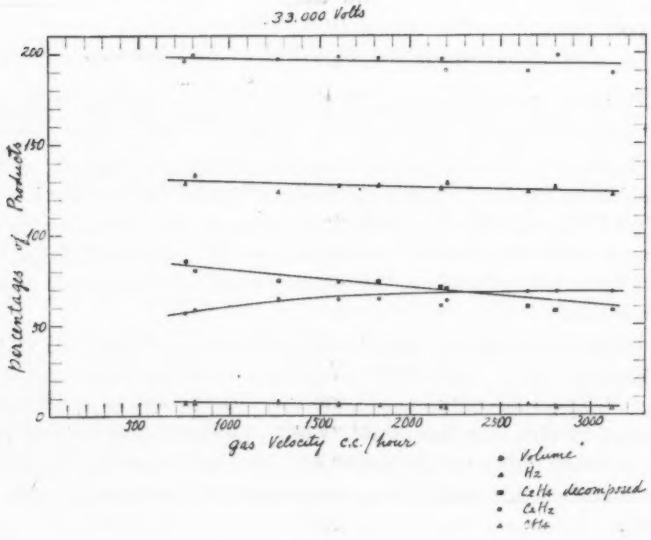

Fig. 3.

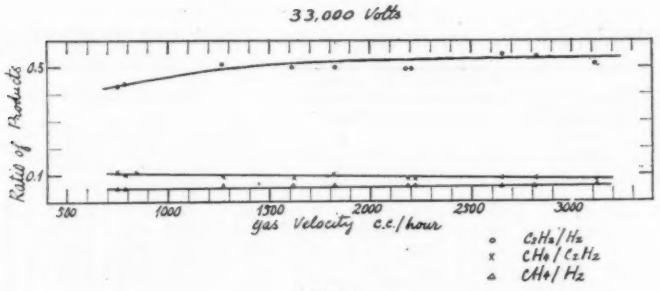

Fig. 4.

The production of hydrogen and methane is increased at a lower gas velocity, the ratio of acetylene to hydrogen in a reaction product increases almost proportionally to the gas velocity but the production of methane to acetylene, and of methane to hydrogen decreases, as indicated in Fig. 4.

The formation of acetylene and methane from ethylene can be explained by assuming that the ethylene molecule produced a radical $=CH_2$ temporarily by the collision of an electron, which was successively converted into radicals $\equiv CH$, $\equiv C$, and they tend to produce acetylene and carbon by polymerisation or methane by hydrogenation.

The fact that the production of acetylene increases with the gas velocity and the absence of ethane in the product certified the theory for the formation of $\equiv CH$ from $=CH_2$, but its hydrogenation is in a minimum degree.

Experimental results for the decomposition of ethane by an electric spark are shown in Table 5 and Fig. 5.

Acetylene, ethylene and hydrogen are the main reaction products and the deposited carbon is similar in nature to that produced by methane.

The production of acetylene and ethylene is almost constant with a gas velocity greater than 1000 c.c. per hour, but that of methane and hydrogen decreases slightly, that is, the ratio of acetylene to hydrogen is constant, but that of methane to ethylene, of methane to acetylene, and of methane to hydrogen, decrease and that of ethylene to acetylene and of ethylene to hydrogen, increase pari passu with the gas velocity, as shown in Fig. 6.

These experimental results indorse the opinion that the radicals $=CH_2$ and $\equiv CH$ are formed from $-CH_3$ dissociated from the ethane molecule, which then proceeds to produce the electric neutral molecules C_2H_4 and C_2H_2.

Table 5.*

Electrode dia. 2.0 cm. Spark gap 2.0 cm. Spark voltage 47,000 volts.

Gas velocity c.c. / hour	Percentage of decomposed ethane	Percentage of gaseous products calculated for decomposed ethane				Ratios of products					
		C_2H_2	C_2H_4	H_2	CH_4	$\frac{C_2H_2}{H_2}$	$\frac{C_2H_4}{H_2}$	$\frac{CH_4}{H_2}$	$\frac{C_2H_4}{C_2H_2}$	$\frac{CH_4}{C_2H_2}$	$\frac{CH_4}{C_2H_4}$
519	64.1	70.7	14.3	226.4	19.2	0.31	0.06	0.09	0.20	0.27	1.34
546	61.1	69.1	15.5	211.2	17.2	0.33	0.07	0.08	0.22	0.25	1.10
750	56.7	66.4	17.4	217.6	16.2	0.31	0.07	0.07	0.26	0.24	0.93
834	48.2	66.7	24.7	209.2	17.9	0.32	0.12	0.09	0.37	0.27	0.73
843	52.9	64.6	23.7	217.0	17.6	0.30	0.11	0.08	0.37	0.27	0.74
1022	52.5	65.8	19.5	208.8	17.8	0.32	0.09	0.09	0.30	0.27	0.91
1290	49.7	62.2	24.9	198.9	17.2	0.31	0.13	0.09	0.40	0.28	0.69
1434	50.4	61.5	20.2	201.2	16.8	0.31	0.10	0.08	0.33	0.27	0.83
1505	47.4	66.5	26.5	217.5	17.2	0.31	0.12	0.08	0.4)	0.26	0.65
1688	48.5	63.1	26.7	197.7	16.7	0.32	0.14	0.08	0.42	0.26	0.63
1693	44.2	66.7	25.7	221.5	18.1	0.30	0.12	0.08	0.39	0.27	0.70
1966	45.6	59.4	24.5	184.9	16.2	0.32	0.13	0.09	0.41	0.27	0.66
2228	39.1	61.7	30.3	192.8	15.7	0.32	0 16	0.08	0.49	0.25	0.52
2662	37.8	64.4	28.1	206.5	16.9	0.31	0.14	0.08	0.44	0.26	0.60
3247	39.8	62.3	26.8	194.5	15.3	0.32	0.14	0.08	0.43	0.26	0.57

* The total percentage of all the gaseous products become greater than 300%, indicating that, among the products, many higher hydrocarbons, such as propane and butane, are formed during the decomposition of the methane. For this reason we understand that the percentages of decomposed ethane must be really more abundant than the represented value for its behavior contrast with methane.

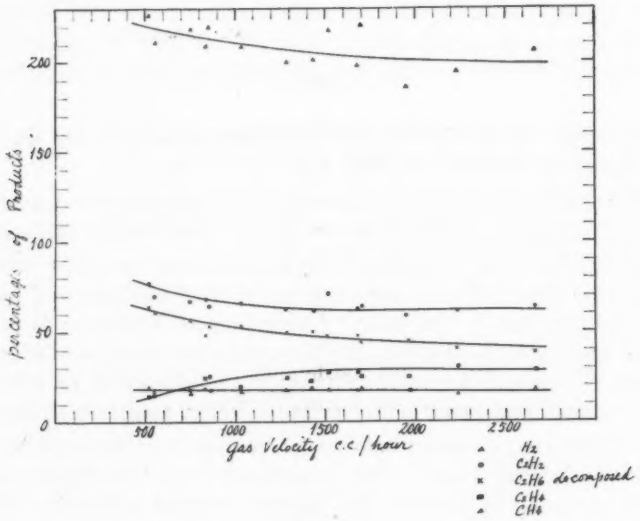

Fig. 5.

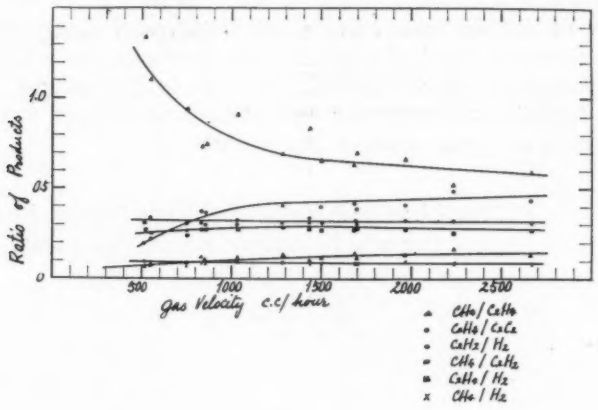

Fig. 6.

When reference is made to the investigation by Lind[1] for the decomposition of propane and butane by the action of α-radiation, the production of the higher hydrocarbons such as benzene in the writer's case is suspected with a great possibility, and further investigation into this interesting subject will surely be fruitful of results.

Conclusions.

Several stream experiments were carried out with methane, ethylene and ethane at varying spark voltages and at different gas velocity.

Considering the experimental results, the radicals ($-CH_2$), ($=CH_2$), ($\equiv CH$) and ($\equiv C$), are supposed to be formed temporarily from methane differing in the yield according to the strength of the electric current, and the rate of the gas velocity, and these radicals, polymerising with one another or combining with activated hydrogen, would produce ethane, ethylene, acetylene, methane and carbon. The polymerisation of the radical ($\equiv CH$), into acetylene is favorable under the experimental conditions, and the formation of benzene or higher hydrocarbons is in full force or promising.

In conclusion, the writer's thanks are due to Director Vice-Admiral S. Kishimoto, for permission to publish these results, and also he is desirous

(1) *J. Am. Chem. Soc.*, **48** (1926), 2335.

of making grateful acknowledgement to Vice-Admiral G. Yamashita, former Director of the Imperial Naval Fuel Depot, and Engineer-Captain Viscount M. Kawase, Chief of the Scientific Research and Experimental Branch for promoting this investigation, and also to Professor S. Komatsu of the Kyoto Imperial University for his invaluable advice and neverfailing encouragement in the prosecution of this research.

The Scientific Research and Experimental Branch,
Imperial Naval Fuel Depot, Tokuyama.

Feb, 1929
see errata
V.5, P.366